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# Effect of As Passivation on Vapor-Phase Epitaxial Growth of Ge on (211)Si as a Buffer Layer for CdTe Epitaxy

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We report an investigation of epitaxial germanium grown by chemical vapor deposition (CVD) on arsenic-terminated (211)Si, which is the preferred substrate in the USA for fabrication of night-vision devices based on mercury cadmium telluride (MCT) grown by molecular-beam epitaxy (MBE). The films were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), cross-sectional transmission electron microscopy (XTEM), and x-ray diffraction (XRD). Arsenic passivation was found to be effective in preventing cross-contamination of unwanted residual species present inside the reactor chamber and also in prolonging the evolution of layer-by-layer growth of Ge for significantly more monolayers than on nonpassivated Si. The two-dimensional (2D) to three-dimensional (3D) transition resulted in Ge islands, the density and morphology of which showed a clear distinction between passivated and nonpassivated (211)Si. Finally, thick Ge layers (~250 nm) were grown at 525°C and 675°C with and without As passivation, where the layers grown with As passivation resulted in higher crystal quality and smooth surface morphology.

**Key words:** Germanium, epitaxy, chemical vapor deposition (CVD), arsenic passivation, (211)Si

## INTRODUCTION

Growth of low-defect-density Ge/Si heterojunctions is of significant importance for many applications, including optoelectronic devices. A major advantage of Ge is its compatibility with conventional Si technology, which makes it suitable for use as a buffer layer in certain material systems. One such area is the use of Ge/Si as an alternate substrate for the growth of CdTe/HgCdTe used in focal-plane arrays (FPAs). (211)Si is the preferred starting substrate in the USA, as it has been observed that CdTe grown on it by molecular-beam epitaxy (MBE) is immune to the formation of twins and hillocks.[1] Chemical vapor deposition (CVD) growth of CdTe directly on Si is possible but difficult due to the presence of Si native oxide. In this context, Ge is better than Si since its surface preparation is easier, and it probably represents the best alternative to Si. Moreover, good-quality CdTe on bulk (211)Ge substrates has been demonstrated earlier.[2,3] More recently, epitaxial (211)B CdTe has been obtained on Ge/Si by metalorganic vapor-phase epitaxy, but the surface morphology of such layers was still poorer compared with layers grown by MBE.[4] These results motivated us to study the evolution of Ge epitaxy and growth of thick (~250 nm to 300 nm) Ge on (211)Si by CVD.

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The quality of epitaxial Ge for device applications is invariably determined by the surface smoothness and by the density of threading dislocations (TDs). Due to the nearly 4.2% lattice mismatch between Ge and Si, growth normally occurs by Stranski–Krastanov (2D to 3D transition) mode, making the generation of misfit and other defects inevitable.[5] Studying the evolution of Ge epitaxy may help to determine optimum conditions for reducing islanding and promoting planar growth, which ultimately may aid in obtaining a high-quality Ge layer. To date, most of the work published on Ge epitaxy has been on (100)Si and (111)Si. Different techniques of defect reduction such as substrate surface passivation, substrate patterning, thermal annealing, and growing Ge on a thin chemical oxide of Si by a "touchdown process" have been attempted.[6–9] The studies invariably have attributed the sudden change in aspect ratio that occurs at the onset of island evolution to strain relaxation and generation of defects. Only two studies relevant to Ge growth on (211)Si are available in the literature, with Ge growth achieved using MBE in both.[10,11] Use of a suitable surfactant (viz. arsenic) has been shown to inhibit island generation up to a few monolayers significantly more compared with growth on nonpassivated (211)Si.[11] In this work, we report on the evolution of Ge on As-passivated (211)Si substrates by CVD. This is the first time that epitaxial Ge grown on As-passivated (211)Si by CVD has been characterized with the objective of obtaining high crystal quality and a smooth epilayer for subsequent growth of (211)B CdTe.

## EXPERIMENTAL PROCEDURES

All the samples were grown in a custom-built low-pressure vertical cold-wall CVD reactor equipped with a rotating quartz heater/substrate holder. Three-inch *n*-type (211)Si nominal wafers were used in all growth runs, having been cleaned by a modified RCA procedure. In brief, the wafers were degreased using organic solvents, followed by cleaning in a 1:1:4 (v/v) mixture of $NH_4OH$, $H_2O_2$, and water at 90°C for 10 min before dipping in a 1:10 mixture of HF and water for 10 s. The wafers were subsequently dipped in 1:1:4 mixture of $H_2SO_4$, $H_2O_2$, and water at 90°C for 10 min and again in 1:10 HF solution for 10 s. Finally, the wafers were dried thoroughly before loading into the reactor and stabilizing to the growth conditions in $H_2$ flow. Diluted germane gas (1% $GeH_4$ in $H_2$) was the precursor for Ge growth. The reactions were carried out at temperatures between 525°C and 675°C, with the reactor pressure, $GeH_4$ partial pressure, and total $H_2$ carrier flow kept constant at 500 torr, 0.12 torr, and 2,500 sccm, respectively. The typical growth procedure consisted of the following sequence: (1) After loading the sample, the reactor temperature was ramped up to the growth temperature under a flow of $H_2$ carrier gas and tertiarybutyl arsine (TBAs) at a mole fraction of $2.4 \times 10^{-4}$ (when As passivation was used), which was the metalorganic precursor for As. (2) After stabilizing the pressure and temperature for a total of 15 min, TBAs was vented and germane was introduced to initiate Ge growth. At the end of the growth period, the reactor was cooled down under TBAs flux until the temperature reached 275°C. Ge (~250 nm thick) was grown at 675°C for the single-step growth process. For two-step growth, a thin nucleating layer was grown first at 525°C, followed by thicker growth at 675°C. Scanning electron microscopy (SEM) was used to measure the thickness of the epilayers. The surface morphology of the grown samples was analyzed using a Veeco Dimension 3100 atomic force microscope in tapping mode. The interface between Ge and Si was analyzed by a JEOL 2010F transmission electron microscope, for which select cross-sectional samples were prepared by mechanical tripod polishing followed by low-temperature ion milling at 10° and low voltage until hole perforation was achieved. The microscope was operated at 200 keV, and imaging was done using both bright- and dark-field diffraction contrasts. The crystal quality of Ge epilayers was analyzed using a Bruker AXS D8 Discover x-ray diffractometer.

## RESULTS AND DISCUSSION

The surface treatment of Si is found to be critical for obtaining good surface morphology of Ge layers. The modified RCA cleaning procedure of the Si substrate followed in the study, with HF treatment as the last step, creates a H-terminated surface.[12–14] However, in a typical CVD reactor with multiple reactant sources, a critical issue is cross-contamination of the starting substrate during heat up with residual reactants present inside the reactor, as a consequence of the "memory effect." The reactor used in the present study had precursors of the following elemental species: Ge, Cd, Te, As, and Zn. Residual Te present inside the reactor chamber was found to react with the Si surface, causing small, nanoscale features all over the wafer, which acted as spurious nucleation sites for subsequent epitaxial growth. Figure 1a shows the surface morphology of (211)Si obtained by atomic force microscopy (AFM) after heating the substrate in hydrogen in the reactor to 525°C for 15 min without introducing any of the precursors. The most likely scenario is that adsorbed hydrogen from the Si surface leaves and the nonpassivated Si reacts with the residual Te in the reactor. Indeed, x-ray photoelectron spectroscopy (XPS) analysis (Fig. 2a) confirmed the presence of Te and Si-Te reaction products on the surface. The results were significantly different when TBAs was introduced during ramping up of the reactor temperature to the desired values. Figure 1b shows an AFM surface plot of a Si wafer heated in the presence of TBAs flow under typical reactor conditions, indicating that As passivation prevented residual Te from attacking the Si surface. The corresponding

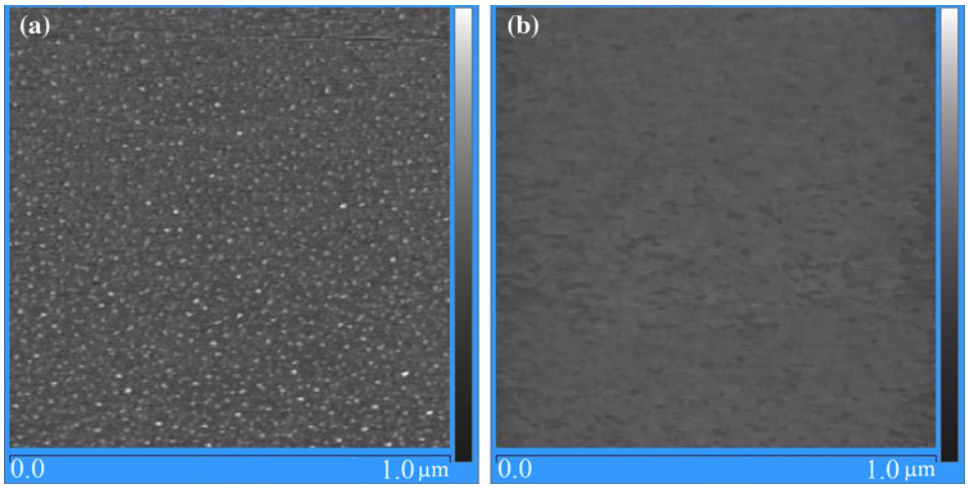


Fig. 1. AFM surface plot of (a) (211)Si surface without TBAs treatment and (b) (211)Si surface treated with TBAs during the ramp up and stabilization steps. The vertical greyscale is 6 nm in both images. With TBAs treatment, no Te surface attack is observed. Typical reactor conditions were 525°C, 100 torr, and $H_2$ flow rate of 2.5 l/min with a 15 min stabilization period.

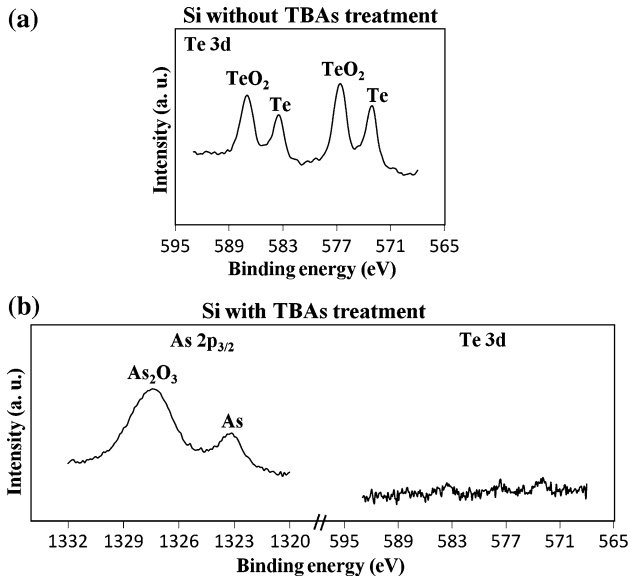


Fig. 2. (a) Te 3d XPS spectrum of (211)Si without TBAs flow during stabilization. A shift in the binding energy can be seen corresponding to elemental Te and $TeO_2$. (b) As $2p_{3/2}$ and Te 3d spectrum of a Si sample with TBAs flow during stabilization, confirming the presence of As and absence of Te due to As passivation.

XPS analysis of the wafer is shown in Fig. 2b, with the Te 3d and As $2p_{3/2}$ spectra confirming the presence of As and absence of Te in the TBAs-treated (211)Si wafer. The oxides of As and Te observed in the XPS signatures may have been formed during the time between unloading the samples and conducting the XPS measurements, when the samples were exposed to the atmosphere. XPS analysis confirmed that TBAs treatment of (211)Si before initiation of Ge growth helped to protect the Si surface from cross-contamination.

Growth of thin Ge on As-passivated (211)Si was carried out next at 525°C for various times, and AFM surface analysis was done to study the morphology of Ge evolution. Figure 3a and b show AFM surface plots of Ge grown on As-passivated (211)Si surface for periods of 5 min and 10 min, respectively. Spectroscopic ellipsometry was used to verify the presence of Ge, and the analysis gave a Ge thickness value of $1.0 \pm 0.1$ nm and $1.7 \pm 0.2$ nm for growth durations of 5 min and 10 min, respectively. The root-mean-square (RMS) roughness values of the films were found to be 0.12 nm and 0.2 nm for Ge grown for 5 min and 10 min, respectively, indicating smooth, ultrathin Ge layers. Rutherford backscattering spectrometry (RBS) further confirmed the presence of thin Ge on (211)Si. It can therefore be said that Ge grows layer-by-layer on As-passivated (211)Si up to a greater thickness compared with growth on nonpassivated (211)Si, for which abrupt Ge islands evolved as early as 40 s after $GeH_4$ exposure under the same reactor conditions (image not shown here). However, even in the case of Ge on As-passivated (211)Si, after 12 min of growth, a catastrophic change from layer-by-layer to island evolution took place, suggesting a Stranski–Krastanov growth mode for Ge on As-passivated (211)Si. Figure 4 shows a scanning electron microscopy (SEM) image of Ge islands after growth for 15 min. The islands were invariably irregular hexagonal in shape with the height ranging between 30 nm and 35 nm and the base width between 90 nm and 110 nm. In contrast to the islands that evolved on nonpassivated Si, the Ge islands on As-passivated (211)Si were larger in size and less dense in their distribution. This is probably a direct consequence of As passivation causing much less active sites to be available on the surface for Ge nucleation. As reported earlier for the case of (211)Si passivated in a MBE system, it is believed that As passivates the Si atoms on the terrace sites which have a single dangling bond but does not coordinate

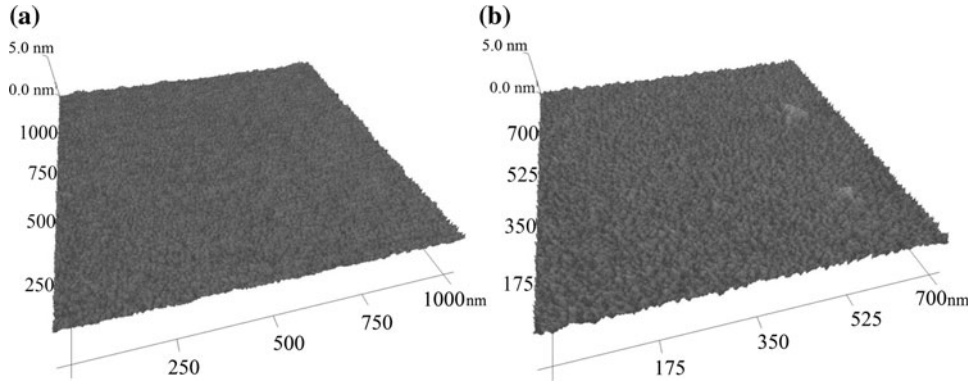


Fig. 3. AFM surface plots of Ge grown on As-treated (211)Si for time periods of (a) 5 min and (b) 10 min. It can be seen that Ge grows layer-by-layer, resulting in a very thin Ge film.

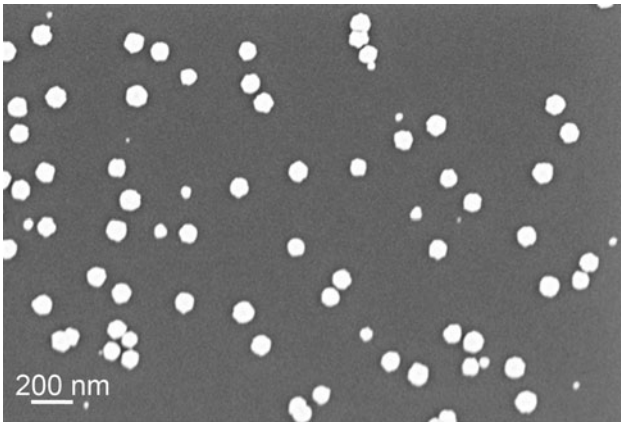


Fig. 4. SEM image of Ge islands on TBAs-treated (211)Si after 15 min of growth at 525°C, 500 torr, 2.5 l/min total $H_2$ flow, and $GeH_4$ mol fraction of $2.4 \times 10^{-4}$. Irregular hexagonal footprints of the islands with a height of 30 nm to 35 nm and base width of 90 nm to 110 nm were invariably observed.

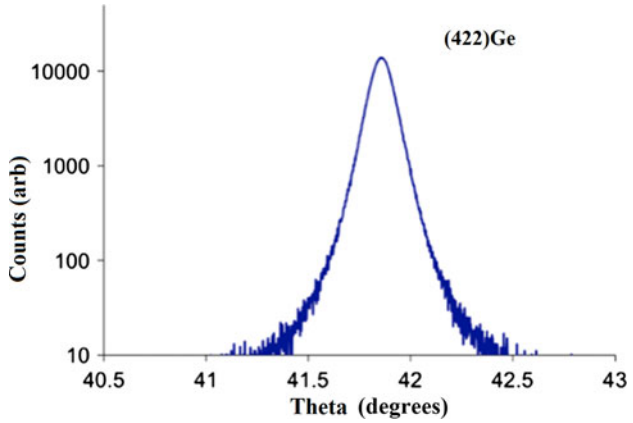


Fig. 5. XRD rocking curve of the (422)Ge peak for the case of growth on As-passivated (211)Si. The FWHM of the peak is 400 arc-s for a film thickness of ~240 nm.

with the Si atoms on the step edges which possess two dangling bonds.[11,15–17] The net effect of this is a reduction in the surface free energy and the surface also becomes resistant to Te contamination. Tellurium may stick at sites not passivated by As, but the detection levels of Te XPS signatures may not be low enough (around noise level) to confirm its presence on As-passivated (211)Si.

A thicker Ge layer (~250 nm) was grown for the main purpose of using it as a buffer layer for subsequent growth of (211)B CdTe. In general, it is observed that higher growth temperatures give better crystal quality but rougher surface morphologies. However in our previous study, we found that a two-step procedure in which a thin nucleation layer (~50 nm) of Ge grown at 525°C followed by thicker growth at 675°C resulted in reasonably good-quality Ge with good surface morphology. In this study, we compared this with the layers grown on an As-passivated (211)Si surface. The x-ray diffraction (XRD) rocking curve of (422)Ge of one such film grown on As-passivated (211)Si is shown in Fig. 5, the analysis of which gave full-width at half-maximum (FWHM) values invariably around 400 arc-s. In contrast, FWHM rocking curve values were around 600 arc-s for samples grown on nonpassivated (211)Si, thus suggesting a significant improvement in crystal quality due to As passivation. The AFM plot of the surface of a Ge epilayer on As-(211)Si showed streaky features oriented along the ⟨110⟩ direction (Fig. 6) which corresponded to the direction of the surface step edges of the (211)Si. The RMS roughness values of the films were around 0.5 nm and 1 nm, respectively, for Ge grown on Si with and without As passivation, indicating a slight decrease in roughness due to passivation.

Cross-sectional transmission electron microscopy (XTEM) analysis was done to understand the role played by As at the interface. Figure 7a and b show cross-section bright-field TEM images of Ge epilayers on (211)Si with and without TBAs flow, respectively. Figure 7a and b are imaged along the $[11\bar{1}]$ and $[11\bar{2}]$ zone axis, respectively. Although it would be preferential to image both samples along the same zone axis, visibility conditions allow threading dislocations for both conditions. In

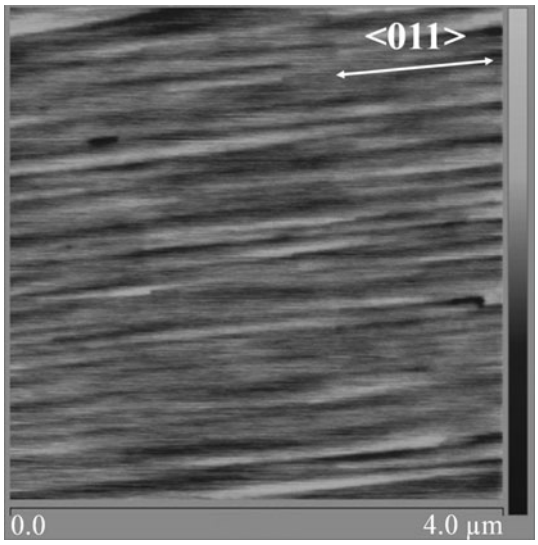


Fig. 6. AFM surface plot of a 250-nm-thick Ge epilayer grown on As-passivated (211)Si. The RMS roughness value of 0.5 nm suggests a relatively smooth epilayer. The vertical color scale is 8 nm.

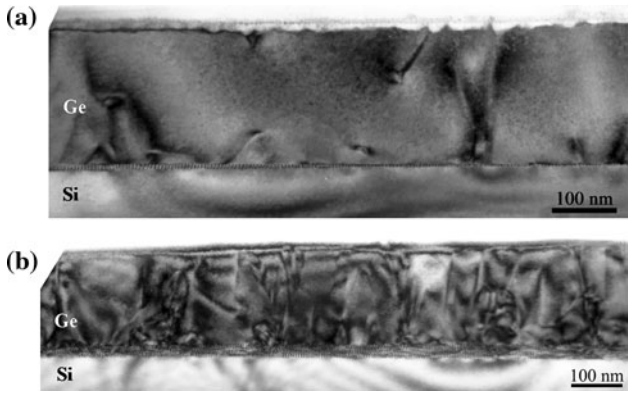


Fig. 7. XTEM bright-field images showing (a) epitaxial Ge on TBAs-treated (211)Si and (b) epitaxial Ge on nonpassivated (211)Si, showing a difference in defect density between the two cases.

Fig. 7b, the $[11\bar{2}]$ zone axis is not orthogonal to the [211] growth direction. However, the projection of the [211] direction onto the $[11\bar{2}]$ plane is perpendicular to the substrate/interface horizontal boundary seen in the image. The $[11\bar{2}]$ zone axis was chosen due to the way in which the sample had been cut. From the TEM analysis, we see a marked difference of at least one order of magnitude in the TD density between the two samples. Both samples show a highly visible array of misfit dislocations at the interface.

## CONCLUSIONS

Epitaxial growth of Ge on As-passivated (211)Si by CVD was achieved and characterized for the first time, with the intention of using the Ge/(211)Si substrates for subsequent growth of (211)B CdTe. Passivation was done using TBAs as a metalorganic precursor of As. TBAs treatment also prevented cross-contamination of the Si surface by residual Te present inside the reactor chamber. A comparison between Ge growth on passivated and nonpassivated (211)Si revealed that passivation helped in prolonging the layer-by-layer growth for a few monolayers. Interestingly, the layer-to-island transformation resulted mostly in hexagonal-shaped islands having an aspect ratio (defined as the ratio of height to the base width of the islands) of ~0.33, which we believe have potential as starting substrates for nanoheteroepitaxial growth of (211)CdTe. Finally, growth of a 250-nm-thick Ge epilayer was achieved by a two-step procedure that gave a FWHM XRD rocking curve value of 400 arc-s and a RMS roughness of 0.5 nm. XTEM analysis showed that As passivation resulted in a decrease in TD density in the Ge layer compared with growth on nonpassivated Si. We believe that further optimization of the growth conditions including annealing could further improve the crystal quality.

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